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Amidophosphine–Borane Complexes of Alkali Metals and the Heavier Alkaline-Earth Metals: Syntheses and Structural Studies

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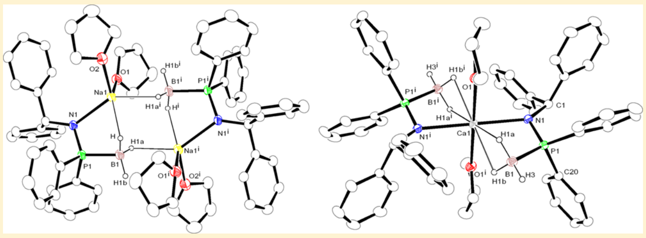
Supporting Information

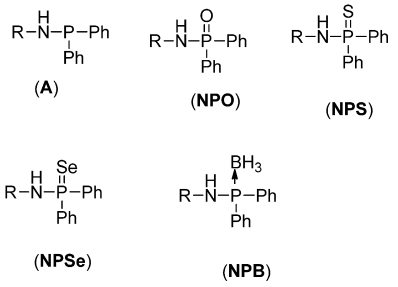


ABSTRACT: The *N*-benzhydrylamido-1,1-diphenylphosphine–borane ligand [$Ph_2P(BH_3)NH(CHPh_2)$] (**1-H**) has been prepared via the reaction of an equimolar ratio of the phosphine amine [$Ph_2PNH(CHPh_2)$] and the borane adduct [$BH_3{\cdot}SMe_2$] at an ambient temperature. The reaction of **1-H** with ((trimethylsilyl)methyl)lithium (neosilyllithium), [$LiCH_2SiMe_3$], afforded a three-membered lithium amidophosphine–borane complex with the composition ([η^2-$Ph_2CHNP(BH_3)Ph_2$)Li(THF)$_2$] (**2**). Analogous reactions with sodium and potassium bis(trimethylsilyl)amides at ambient temperature yielded the respective alkali-metal amidophosphine–borane complexes [$\{(Ph_2CHNP(BH_3)Ph_2)Na(THF)_2\}_2$] (**3**) and [$\{(Ph_2CHNP(BH_3)Ph_2)K(THF)_2\}_2$] (**4**), with the loss of hexamethyldisilazane, [$(Me_3Si)_2NH$]. The corresponding heavier alkaline-earth-metal complexes [$M(THF)_2\{Ph_2P(BH_3)N(CHPh_2)\}_2$] (M = Ca (**5**), Sr (**6**), Ba (**7**)) can be obtained via the reaction of [$M\{N(SiMe_3)_2\}_2(THF)_n$] (M = Ca, Sr, Ba) and **1-H**. The metal complexes **5**–**7** can also be prepared via a salt metathesis route, where the alkali-metal salts **3** and **4** were reacted with the respective metal diiodides in THF at ambient temperature. The molecular structures of **1-H** and **2**–**7** have been established by X-ray diffraction analyses, and from the solid-state structures of **3**–**7**, it was confirmed that, in all of the compounds, the metal ions are chelated through the nitrogen atom and the hydrogen atoms of the borane group of ligand **1-H**.

INTRODUCTION

Homoleptic and heteroleptic alkaline-earth-metal complexes are attractive to organometallic chemists because of their oxophilic and electropositive nature in comparison to those complexes formed from early d transition metals.[1] The alkaline-earth-metal complexes have recently been employed in various catalytic applications, including the ring-opening polymerization of various cyclic esters,[2,3] the polymerization of styrene and dienes,[4] and the hydroamination and hydrophosphination of alkenes and alkynes.[5] Determining the structures and reactivities of alkaline-earth-metal species is an important step toward the design and development of efficient catalysts; however, full realization of the catalytic potential of these elements still requires substantial advances in the understanding of their basic coordination and organometallic chemistry. To stabilize these extremely oxophilic and electropositive metals, a wide variety of nitrogen-based ancillary ligands, such as tris(pyrazolyl)borates,[6] aminotroponiminates,[7] β-diketiminates,[8] iminopyrroles,[9] and 1,4-diaza-1,3-butadiene,[10] have been introduced to prepare well-defined alkaline-earth-metal complexes, revealing that the catalytic activity and the selectivity of the alkaline-earth-metal complexes can be controlled via a well-defined nitrogen-based ligand architecture. We have recently introduced the series of phosphine amines [Ph_2PNHR] (**A**; R = 2,6-$Me_2C_6H_3$, $CHPh_2$, CPh_3) and their chalcogen derivatives [$Ph_2P(O)NHR$] (**NPO**), [$Ph_2P(S)NHR$] (**NPS**), and [$Ph_2P(Se)NHR$] (**NPSe**) (Chart 1) into the chemistry of alkali metals and the heavier alkaline-earth metals.[11] Phosphine amine **A** can coordinate to metals through the nitrogen and phosphorus atoms, resulting in a highly strained three-membered metallacycle, as reported by Roesky

Chart 1. Phosphine Amine Ligands and Their Chalcogenides and Borane Compounds



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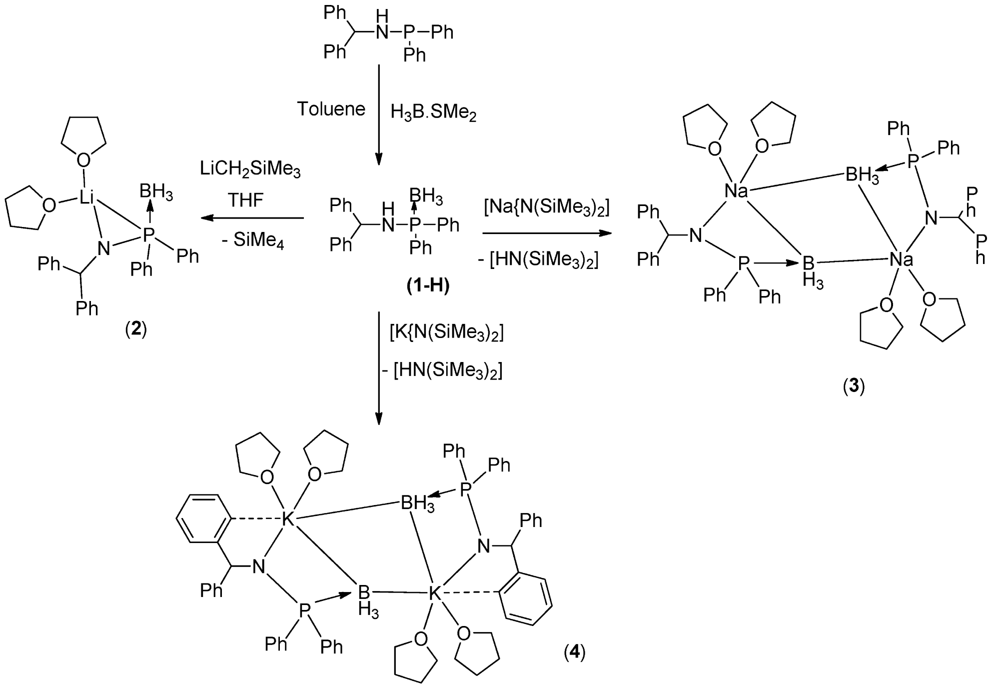
Scheme 1. Synthesis of 1-H and the Corresponding Alkali-Metal Complexes



and others.[12,13] The phosphine amine chalcogenides **NPO**, **NPS**, and **NPSe** can form either a four-membered metallacycle, if the nitrogen and the chalcogen atoms (O, S, Se) coordinate to the metal center, or two fused three-membered metallacycles to stabilize the metal complexes, which is what we observed in alkali-metal and heavier alkaline-earth-metal complexes.[11] Thus, due to the presence of three adjacent potential donor atoms, the polymetallacyclic structural motif of the metal complexes was explored.

The basicity of the nitrogen atom adjacent to the phosphorus atom in the amidophosphines **A** has remained the driving factor in the ability of the nitrogen and the phosphorus to effectively coordinate to an electron-deficient group. It is well accepted that in acyclic phosphineamines the tricoordinate nitrogen atom assumes a planar configuration with respect to its substituents and thus demonstrates diminished basicity due to enhanced N(pπ)–P(dπ) bonding.[14−16] From these literature reports and the phosphine amines available to us, we decided to synthesize the amidophosphine–borane adduct to exploit the chelating behavior of amidophosphines in alkali-metal and alkaline-earth-metal chemistry. This idea will also help us to extend our ligand skeleton as **NPB** (vide infra) and, in a similar fashion, as **NPO**, **NPS**, and **NPSe** (Chart 1). The complexation of a divalent metal by the **NPB** ligand (**1-H**) potentially leads to complexes that are isostructural with amidophosphine–chalcogenide divalent complexes of the type $[\{\eta^2\text{-}Ph_2P(X)N(CHPh_2)\}_2M(THF)_2]$.[11] Very recently, the Verdaguer and Kolodiazhnyi groups reported a series of chiral aminophosphine–borane compounds and their applications in asymmetric catalysis and hydrogenolysis.[17] However, reports of their use as coordinating ligands toward alkali metals and alkaline-earth metals are not available to date. We envision that **1-H** can be deprotonated to generate the monoanionic compound $\{(Ph_2CHNP(BH_3)Ph_2)\}^-$, which can coordinate to the metal center. Gaumont and co-workers reported that copper(I) complexes using an anionic phosphido–borane adduct can be used as precatalysts for the formation of phosphorus–carbon bonds.[18] Most of the structurally characterized complexes in this category can be classified into two classes: in alkali-metal complexes, the hard metal center is chelated by the borane hydrogen atoms of the ligand, and in transition-metal complexes, the soft phosphorus atom shows a preference to bind with the relatively softer metal center.[19] It has also been reported that the lithium phosphine–borane complex is diatopic in nature and can be used to reduce aldehydes to generate the corresponding phosphine–borane-substituted alcohols at elevated temperatures.[20] However, the vast potential of this field of chemistry is still underdeveloped.

In this context, alkali-metal amidophosphine–borane complexes with the compositions $[(\eta^2\text{-}Ph_2CHNP(BH_3)Ph_2)Li(THF)_2]$ (**2**), $[\{(\eta^2\text{-}Ph_2C\text{-}HNP(BH_3)Ph_2)Na(THF)_2\}_2]$ (**3**), and $[\{(\eta^2\text{-}Ph_2CHNP(BH_3)Ph_2)K(THF)_2\}_2]$ (**4**) are presented. The heavier alkaline-earth-metal complexes $[M(THF)_2\{Ph_2P(BH_3)N(CHPh_2)\}_2]$ (M = Ca (**5**), Sr (**6**), Ba (**7**)) are also reported herein and can be prepared with high yields and purities by two synthetic routes. The full accounts of two synthetic routes and the solid-state structures of all the complexes are presented.

■ RESULTS AND DISCUSSION

Ligand Synthesis. The ligand **1-H** has been isolated as a white precipitate from the reaction of the phosphine amine $[Ph_2PNH(CHPh_2)]$ and the borane adduct $[BH_3{\cdot}SMe_2]$ at an ambient temperature in a 1:1 molar ratio (Scheme 1).[21] The formation of the amidophosphine–borane **1-H** from the phosphine amine $[Ph_2PNH(CHPh_2)]$ can be easily followed by ^1H NMR spectroscopy, because additional resonances are observed as a broad signal at 1.17 ppm for the borane (BH_3) group attached to the phosphorus atom. In the ^1H NMR spectrum, the resonances of the amidophosphine moiety in **1-H** are only slightly shifted in comparison to those reported for the phosphine amine starting material.[11] The doublet at 5.45 ppm can be assigned to the methine proton of the CH group attached to the nitrogen, and this is very close to the peak (5.25

ppm) of the ligand precursor. Another broad signal at 2.83 ppm (2.52 ppm for the ligand precursor) corresponds to the amido group of **1-H**. In the $^{31}P\{^1H\}$ NMR spectrum, a doublet is observed at 56.8 ppm, which is shifted significantly to low field in comparison to the signal (35.2 ppm) of the ligand precursor. A coupling constant of 85.8 Hz is observed, which can be assigned as the J_{PB} coupling between the ^{31}P and ^{11}B atoms adjacent to each other. The J_{PB} value is similar to the reported value (80.1 Hz) for $[(R_2PBX_2)_4]$ ($R = CH_3$, $X = H$).[22] In the $^{11}B\{^1H\}$ NMR spectrum, we obtained a doublet at −38.1 ppm for the BH_3 group. These observations clearly indicate that the BH_3 group forms the phosphine−borane adduct rather than the amido−borane adduct, which is usually formed in homogeneous middle- or late-transition-metal catalysis.[23] The characteristic signal for P−B bond stretching at 602 cm^{-1} in the FT-IR spectra was observed along with another characteristic signal at 2383 cm^{-1} assigned as the B−H stretching frequency. These values are in agreement with the values reported in the literature.[24] The molecular structure of ligand **1-H** has been established by single-crystal X-ray diffraction analysis. Compound **1-H** crystallizes in the triclinic space group $P\bar{1}$ and has two independent molecules in the unit cell (Figure 1). The details of the structural parameters of the crystal structure of **1-H** are given in the Supporting Information. The P1−B1 bond distance in **1-H** (1.918(6) Å) is in agreement with the reported value of 2.1019(8) Å for $[\{Ph_2P(BH_3)\}_2CH_2]$ and can be considered a phosphorus−boron dative bond. The bond distances P1−N1 (1.638(3) Å) and C1−N1 (1.468(5) Å) are also similar to those of the phosphine amine compound $[Ph_2PNH(CHPh_2)]$ (P1−N1 = 1.673(6) Å and C1−N1 = 1.453(8) Å), as we previously observed.[11]

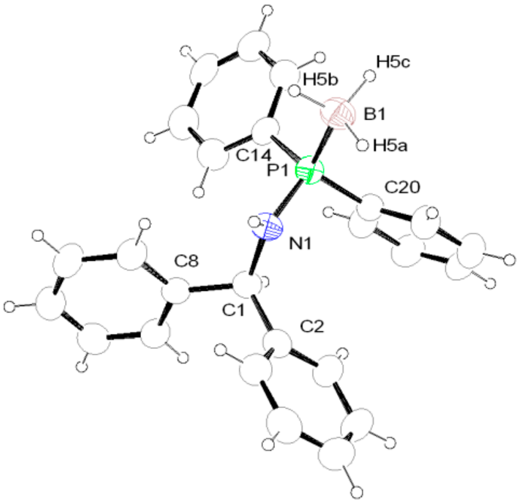


Figure 1. ORTEP drawing of **1-H** with thermal displacement parameters drawn at the 30% probability level. Selected bond lengths (Å) and bond angles (deg): P1−N1 = 1.638(3), P1−B1 = 1.918(6), P1−C14 = 1.812(4), P1−C20 = 1.815(4), N1−C1 = 1.468(5), C1−C2 = 1.537(6), C1−C8 = 1.532(6); B1−P1−N1 = 107.8(3), B1−P1−C14 = 112.7(3), B1−P1−C20 = 115.4(3), P1−N1−C1 = 127.5(3), N1−C1−C8 = 113.4(3), N1−C1−C2 = 110.4(3).

Synthesis and Characterization of the Alkali-Metal Complexes. Ligand **1-H** was reacted with ((trimethylsilyl)-methyl)lithium in THF at ambient temperature in a 1:1 molar ratio to afford a lithium amidophosphine−borane complex with the composition $[\{\eta^2\text{-}Ph_2CHNP(BH_3)Ph_2\}Li(THF)_2]$ (**2**) through the elimination of the volatile tetramethylsilane (Scheme 1).[21] Compound **2** was recrystallized from THF and *n*-pentane (1:2 ratio) and was found to crystallize in the monoclinic space group $P2_1/c$, which has four molecules in the unit cell. The solid-state structure of complex **2** is given in Figure 2. The details of the structural parameters are given in Table S1 in the Supporting Information. The lithium coordination polyhedron of complex **2** is formed by the chelation of the amido nitrogen, the phosphorus atom of the ligand moiety, and two THF molecules. Notably, the borane group does not participate in the coordination to the lithium metal, which can be explained as being due to the smaller size of the lithium metal in comparison to the other metals used in this work. The Li1−N1 distance of 1.971(3) Å is very similar to the lithium−amido bond distances reported in the literature.[25] The Li1−O1 (1.945(3) Å) and Li1−O2 (1.929(3) Å) bond distances are also consistent with reported values. The Li1−P1 distance of 2.925(3) Å is slightly greater than the distances of 2.611(6) and 2.527(3) Å reported for $[[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}SMe)]Li(THF)]_2$ in the literature[25] and can be termed as a very weak interaction between the phosphorus and lithium atoms. Thus, a three-membered metallacycle, Li1−N1−P1, is formed that has the bond angles Li1−P1−N1 = 39.61(7)°, N1−Li1−P1 = 31.50(6)°, and Li1−N1−P1 = 108.88(11)°. Similar three-membered lithium metallacycles can be found in the literature.[25] The P1−B1 distance (1.9199(18) Å) remained unchanged in comparison to that of ligand **1-H** (1.918(6) Å). The ^1H, $^{31}P\{^1H\}$, and $^{11}B\{^1H\}$ NMR spectra also confirmed the solid-state structure of **2**. In the ^1H NMR spectra, a doublet at 5.41 ppm can be assigned to the methine proton of ligand moiety **1** having a coupling constant ($^3J_{HP}$) of 21.5 Hz. The three protons of the free BH_3 group give a broad signal at 1.45 ppm, which is similar to the signal from **1-H**. Coordinated THF signals are also observed as

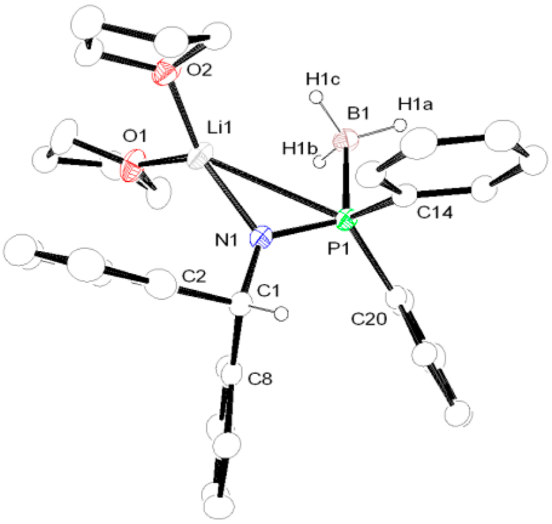


Figure 2. ORTEP drawing of **2** with thermal displacement parameters drawn at the 30% probability level. Hydrogen atoms except (H1, H1a, H1b, H1c) are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): P1−N1 = 1.6155(13), P1−B1 = 1.9199(18), P1−Li1 = 2.925(3), N1−Li1 = 1.971(3), N1−C1 = 1.4648(19), Li1−O1 = 1.945(3), Li1−O2 = 1.929(3), B1−H1a = 1.09(2), B1−H1b = 1.10(2), B1−H1c = 1.08(2); B1−P1−N1 = 108.02(8), B1−P1−Li1 = 69.39(8), P1−Li1−N1 = 31.50(6), P1−N1−Li1 = 108.88(11), O1−Li1−O2 = 106.65(14), P1−N1−C1 = 120.76(10), B1−P1−C14 = 109.87(7), B1−P1−C20 = 111.92(7), Li1−P1−N1 = 39.61(7).

two broad singlets at 3.32 and 1.17 ppm. The proton-decoupled ^{31}P NMR spectrum shows a doublet at 71.1 ppm, which exhibits a significant low-field shift in comparison to the corresponding signal of ligand **1-H** (56.8 ppm). The ^{11}B{^{1}H} NMR spectrum is also informative and shows a doublet signal at −36.1 ppm, which is shifted slightly to low field in comparison to that of the free ligand **1-H** (−38.1 ppm).

The dimeric sodium and potassium amidophosphine−borane complexes with molecular formulas [{(η^2-$Ph_2CHNP(BH_3)$-Ph_2)Na$(THF)_2$}$_2$] (**3**) and [{(η^2-$Ph_2CHNP(BH_3)Ph_2$)K-$(THF)_2$}$_2$] (**4**) were prepared via the reaction of **1-H** and sodium bis(trimethyl)silylamide (or potassium bis(trimethylsilyl)amide in the case of **4**) in THF at ambient temperature through the elimination of volatile bis(trimethylsilyl)amine (Scheme 1). Both of the complexes were characterized by spectroscopic and analytical techniques, and the solid-state structures of complexes **3** and **4** were established by single-crystal X-ray diffraction analyses.

In the ^{1}H NMR spectra of **3** and **4**, the resonance signals are similar, due to their similar structural properties. The characteristic doublet at 5.46 ppm (5.73 ppm for **4**) can be assigned to the methine proton of the CH group attached to the nitrogen having coupling constants ($^{3}J_{PH}$) of 25 Hz (for **3**) and 21.5 Hz (for **4**), and they are shifted slightly to low field in comparison to the corresponding signal (5.45 ppm) of ligand **1-H**. In the ^{31}P{^{1}H} NMR spectra, a doublet is observed at 46.2 ppm (73.2 ppm for **4**). Thus, for complex **3**, the resonance for the phosphorus is shifted slightly to high field, whereas in complex **4**, the resonance of the phosphorus atom is shifted significantly to low field in comparison to that (56.8 ppm) of **1-H**. This result can be attributed to the fact that the phosphorus atom is highly influenced by the electron-deficient borane (BH_3) group attached to it. The doublet signal is caused by the coupling between the ^{31}P and ^{11}B atoms adjacent to each other, and a coupling constant (135.9 Hz for **3**) is observed. In the ^{11}B{^{1}H} NMR spectra, we obtained a broad doublet signal at −34.2 ppm for **3** (−37.4 ppm for **4**), and the broadening is presumably caused by the coupling to the adjacent phosphorus atom. In the FT-IR spectra, the characteristic signal for the P−B bond stretching at 610 cm^{-1} for **3** (607 cm^{-1} for complex **4**) was observed along with another characteristic signal at 2379 cm^{-1} for **3** (2380 cm^{-1} for **4**) assigned as the B−H stretching frequency. These values correspond well with the values (602 and 2383 cm^{-1}) of the neutral ligand **1-H** as well (vide supra).

Single crystals of the sodium and potassium salts **3** and **4** were obtained from a mixture of THF and *n*-pentane, and in the solid state, both the complexes crystallized in the triclinic space group $P\bar{1}$ and had one molecule in the unit cell. The solid-state structures of complexes **3** and **4** are given in Figures 3 and 4, respectively. All of the hydrogen atoms were located in the Fourier difference map and were subsequently refined. In the centrosymmetric molecule **3**, two amidophosphine−borane ligands coordinate to two sodium atoms by one BH_3 group, one phosphorus atom, and one amido nitrogen atom and exhibit a diamond-shaped $Na_2(BH_3)_2$ core with the mean bond angles B1−Na−B1^{i} = 85.73(9)° and Na1−B1−Na1^{i} = 94.27(9)°. The BH_3 borane groups of the two ligands coordinate to the sodium atom in a η^1 fashion with a Na1−B1 bond distance of 2.949(3) Å and a Na1−B1^{i} bond distance of 2.862(3) Å. The P1−Na1 distance of 3.2078(11) Å is slightly longer than the bond distances of 2.9661(17) and 2.9474(16) Å reported for [[{$(Me_3Si)_2CH$}P$(BH_3)(C_6H_4$-2-SMe)]Na(tmeda)]$_\infty$ by Izod and co-workers,[25c,d] and is also larger than the sum of the covalent radii (3.00 Å) of sodium and phosphorus. Thus, it can be concluded that no interaction between the phosphorus and sodium atoms can be observed. In complex **3**, two additional THF molecules are also coordinated to each sodium atom, and the geometry of each sodium atom can best be described as a distorted trigonal bipyramidal having two THF molecules in the apical position. The bond distances Na1−N1 = 2.387(2), Na1−O1 = 2.337 (2), and Na1−O2 = 2.4377(2) Å are in the range of the previously reported values.[11] The P1−B1 distance (1.921(3)Å) remains almost unchanged compared to that of the free ligand **1-H** (1.918(6) Å). If the BH_3 group is considered monodentate, the entire structure consists of three four-membered rings forming a trimetallacyclo [4.2.0.0^{2,5}]-octane structure. To the best of our knowledge, this is the first example of that type of structural motif in sodium complexes using borane groups.[26]

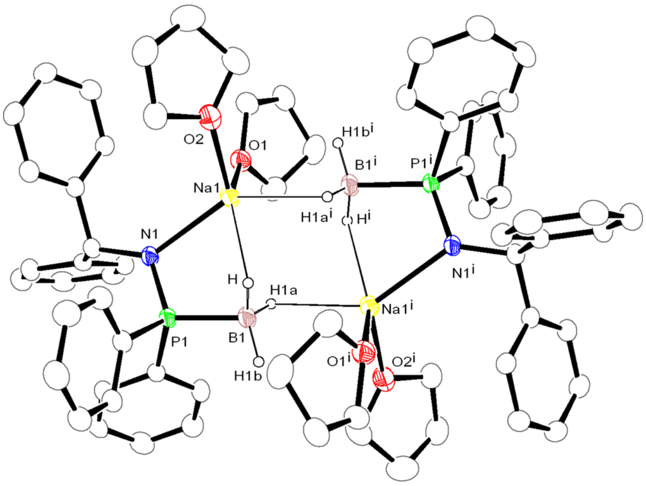


Figure 3. ORTEP drawing of **3** with thermal displacement parameters drawn at the 30% probability level. Hydrogen atoms (except H1a, H1b; H, and H1a^{i}, H1b^{i}, H^{i}) are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): P1−N1 = 1.6060(19), P1−B1 = 1.921(3), P1−Na1 = 3.2078(11), B1−Na1 = 2.949(3), B1^{i}-Na1 = 2.862(3), N1−Na1 = 2.387(2), Na1−O1 = 2.337(2), Na1−O2 = 2.377(2), B1−H = 1.15(3), B1−H1a = 1.07(3), B1−H1b = 1.10(3), Na1−H = 2.57(3); B1−P1−N1 = 110.35(11), P1−B1−Na1 = 79.34(10), P1−B1−Na1^{i} = 170.67(15), P1−N1−Na1 = 105.23(9), O1−Na1−O2 = 106.96(8), B1−Na1−N1 = 64.87(7), B1−Na1−P1 = 36.05(5), P1−Na1−N1 = 28.89(5), O1−Na1−B1 = 127.09(9), O2−Na1−B1 = 125.71(9), O1−Na1−P1 = 118.68(6), O2−Na1−P1 = 122.16(6), N1−Na1−H = 75.5(6), B1−Na1−H = 22.7(6), P1−Na1−H = 48.5(6), H−B1−H1a = 110(2), H−B1−H1b = 115(2), H1a−B1−H1b = 112(2), Na1−B1−Na^{i} = 94.27(9), B1−Na1−B1^{i} = 85.73(9).

The potassium complex **4** is centrosymmetric and dimeric in nature, where each potassium atom is coordinated by two amidodiphenylphosphine−borane ligands, **1**, via one phosphorus atom and one amido nitrogen atom along with one BH_3 group. It exhibits a diamond-shaped $K_2(BH_3)_2$ core with a mean B1−K1−B1^{i} bond angle of 85.68(4) Å and a mean K1−B1−K1^{i} bond angle of 94.32(9)°. Each BH_3 borane group of the two ligands coordinates to two potassium atoms in a η^3 fashion with a K1−B1 bond length of 3.043(3) Å and a K1−B1^{i} bond length of 3.193(4) Å. The P1−K1 bond distance of 3.5148(10) Å is even more elongated in comparison to the P1−Na1 distance (3.2078(11) Å) and is also longer than the sum of the covalent radii (3.45 Å) of potassium and phosphorus.[25d] Each potassium atom is bound to two THF molecules, having

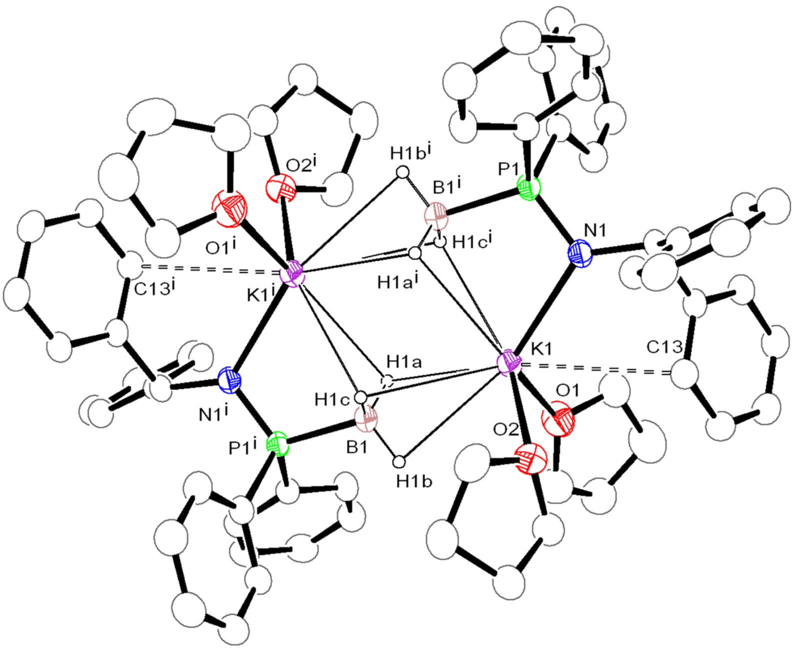
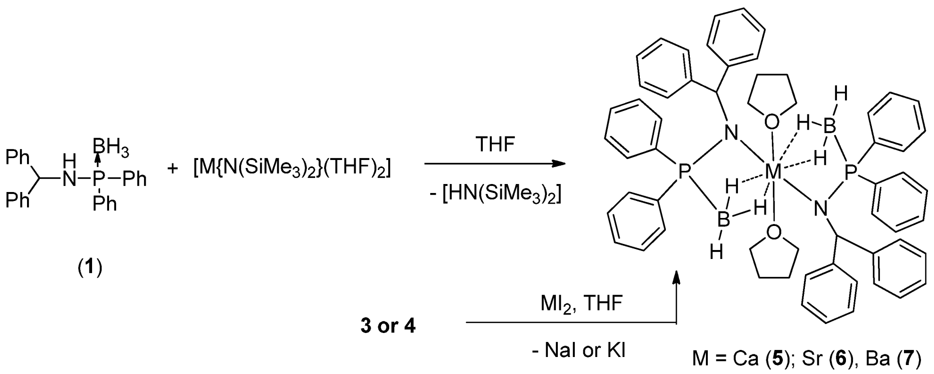


Figure 4. ORTEP drawing of **4** with thermal displacement parameters drawn at the 30% probability level. Hydrogen atoms (except H1a, H1b, H1c and H1a^i, H1b^i and H1c^i) are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): P1−N1 = 1.604(2), P1−B1^i = 1.920(3), P1−K1 = 3.5148(10), B1^i−K1 = 3.192(4), B1−K1 = 3.043(3), N1−K1 = 2.691(2), K1−O1 = 2.713(3), K1−O2 = 2.651(3), K1−C13 = 3.468(3), B1−H1a = 1.09(4), B1−H1b = 1.15(4), B1−H1c = 1.16(3), K1−H1a = 2.69(4), K1−H1b = 2.93(3), K1−H1c = 3.01(3), K1−K1^i = 4.5732(13); B1^i−P1−N1 = 110.73(14), P1^i−B1−K1^i = 82.86(12), P1−N1−K1 = 107.11(11), O1−K1−O2 = 105.99(9), B1^i−K1−N1 = 58.44(8), B1^i−K1−P1 = 32.82(6), P1−K1−N1 = 25.86(5), B1−K1−B1^i = 85.68(9), B1−K1−O1 = 94.50(9), B1−K1−O2 = 89.70(9), H1a−B1−H1b = 106(3), H1a−B1−H1c = 112(3), H1b−B1−H1c = 112(2), K1−B1−K1^i = 94.32(9).

Scheme 2. Syntheses of Alkaline-Earth-Metal Amidophosphine−Borane Complexes 5−7



the bond distances K1−O1 = 2.713(3) Å and K1−O2 = 2.651(3) Å. The P1−B1 distance (1.917(4) Å) remains almost unperturbed in comparison to that of ligand **1** (1.920(3) Å). A short contact between the potassium and one of the phenyl carbon atoms (K1···C13 (3.469(3) Å) is observed, which can be attributed to a remote or secondary M−C interaction. However, in solution, all phenyl protons appear to be equivalent, as observed in the ^{1}H NMR study, presumably due to the dynamic behavior of the complex. Thus, in the solid state, the two additional five-membered metallacycles K1−N1−C1−C8−C13 and K1^i−N1^i−C1^i−C8^i−C13 ^{i} are formed.

Alkaline-Earth-Metal Complexes. The reaction of **1-H** with alkaline-earth-metal bis(trimethylsilyl)amides [M{N(SiMe$_3$)$_2$}$_2$(THF)$_n$] (M = Ca, Sr, Ba) in a 2:1 molar ratio in THF followed by crystallization from THF and *n*-pentane yields the respective heavier alkaline-earth-metal amidophosphine−borane complexes [M(THF)$_2${Ph$_2$P(BH$_3$)N(CHPh$_2$)}$_2$] (M = Ca (**5**), Sr (**6**), Ba (**7**)) at ambient temperatures with the loss of bis(trimethylsilyl)amine, [(Me$_3$Si)$_2$NH]. The same alkaline-earth-metal complexes, **5**−**7**, can also be prepared by a salt metathesis reaction involving **3** or **4** with alkaline-earth-metal diiodides in THF at ambient temperature (Scheme 2).[21] The silylamide route was followed for all three complexes **5**−**7**, whereas both routes were used to prepare the calcium complex **5**. The silylamide route gave higher purity metal complexes in comparison to the salt metathesis reaction.[27] All of the new complexes **5**−**7** were characterized using standard analytical and spectroscopic techniques, and the solid-state structures were established by single-crystal X-ray diffraction analyses.

A strong absorption at 610 cm^{-1} (for **5**), 610 cm^{-1} (for **6**), and 603 cm^{-1} (for **7**) in the FT-IR spectra is evidence of the P−B bond in each complex. The ^{1}H NMR spectra of **5**−**7** in C$_6$D$_6$ are very similar to the spectra recorded for complexes **3** and **4** (vide supra) and reveals time-averaged C_s symmetry in solution. The presence of solvated THF is also indicated by two broad signals: 3.32 and 1.17 ppm for **5**; 3.45 and 1.29 ppm for **6**; 3.38 ppm and 1.24 ppm for **7**. The doublet signals due to the resonance of the methine protons (5.49 ppm for **5**, 5.53 ppm for **6**, and 5.48 ppm for **7**) in the ^{1}H NMR spectra of complexes **5**−**7** remained almost unaffected in comparison to the signals of the free ligand (5.45 ppm) after complex formation with the metals. The coupling between the phosphorus and the methine proton is also evident from their respective coupling constants (23.3 Hz for **5**, 24.5 Hz for **6**, and 22.3 Hz for **7**), which are within the range reported in the literature.[28] The resonance of the three protons attached to the boron atom appeared as a broad signal (1.62 ppm for **5**, 1.63 ppm for **6**, and 1.72 ppm for **7**) in the ^{1}H NMR spectra. In the proton-decoupled ^{31}P NMR spectra, complexes **5**−**7** show only one doublet signal at 46.9 ppm for **5**, 46.3 ppm for **6**, and 46.9 ppm for **7**, respectively, and these values are shifted significantly to high field in comparison to the value for compound **1-H** (56.8 ppm) upon the coordination of calcium, strontium, or barium atoms to the amidophosphine−borane ligand. The phosphorus atoms present in the two $\{Ph_2P(BH_3)N(CHPh_2)\}^-$ moieties are chemically equivalent.

Although there has been ongoing interest in alkaline-earth organometallics[29a] and particularly in the cyclopentadienyl chemistry of these elements,[29b] complexes **5**−**7** represent, to the best of our knowledge, the first amidophosphine−borane alkaline-earth-metal complexes containing three hetero atoms, N, P, and B, adjacent to each other in the ligand. Therefore, their molecular structures in the solid state were determined by X-ray diffraction analysis. The calcium and strontium complexes **5** and **6** crystallize in the triclinic space group $P\bar{1}$ and have one molecule of either **5** or **6** and two THF molecules as solvent in the unit cell. The details of the structural parameters are given in Table S1 in the Supporting Information. The solid-state structures of complexes **5** and **6** are shown in Figures 5 and 6, respectively. Complexes **5** and **6** are isostructural with each other, due to the similar ionic radii for the metal ions (1.00 and 1.18 Å) for a coordination number of 6.[30]

In the centrosymmetric molecule **5**, the metal coordination polyhedron is formed by two monoanionic $\{Ph_2P(BH_3)N(CHPh_2)\}^-$ ligand moieties and two THF molecules, which are trans to each other. Each of the $\{Ph_2P(BH_3)N(CHPh_2)\}^-$ ligands coordinates to the calcium atom via the chelation of one of the amido nitrogen atoms and the BH_3 group. The P−Ca distance of 3.2308(4) Å in **5** is significantly larger than the sum of the covalent radii (3.07 Å) of phosphorus and calcium, which indicates that there is no interaction between these two atoms. The borane (BH_3) group coordinates through the hydrogen atoms in a η^2 fashion and has a Ca1−B1 bond length of 2.850(2) Å. Thus, the $\{Ph_2P(BH_3)N(CHPh_2)\}^-$ group can be considered a pseudo-bidentate ligand. The Ca1−B1 distance is slightly longer than the 2.751(2) Å distance reported for $[[(Me_3Si)_2\{Me_2(BH_3)P\}C]_2Ca(THF)_4]$.[31] The central atom, calcium, adopts a distorted-octahedral geometry due to the coordination of two **1** moieties and two THF molecules. The N1, P1, B1, and Ca1 atoms are not coplanar; rather, a dihedral angle of 10.11° is observed between the planes containing the P1, N1, and Ca1 atoms and the P1, B1, and Ca1 atoms. The Ca1−N1 distance of 2.4534(14) Å is slightly elongated in comparison with the calcium−nitrogen covalent bond distances (2.361(2) and 2.335(2) Å) reported for $[Ca(Dipp_2DAD)(THF)_4]$ ($Dipp_2DAD$ = *N*,*N*′-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene) in the literature[10] but is close to the corresponding distance (2.479(5) Å) of our recently reported complex $[Ca(THF)_2\{Ph_2P(Se)N(CHPh_2)\}_2]$ using the analogous phosphine selenoic amido ligand.[11c] It is noteworthy that the P1−B1 distance (1.921(2) Å) remains almost unperturbed

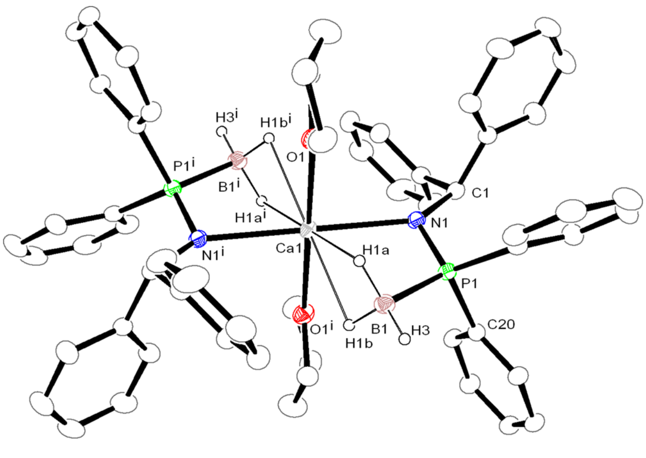


Figure 5. ORTEP drawing of **5** with thermal displacement parameters drawn at the 30% probability level. Hydrogen atoms (except H1a, H1b, H3 and H1a^i, H1b^i, H3^i) are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): P1−N1 = 1.6217(14), P1−B1 = 1.921(2), P1−Ca1 = 3.2308(4), N1−Ca1 = 2.4534(14), B1−Ca1 = 2.850(2), Ca1−O1 = 2.5111(12), Ca1−H1a = 2.4961, Ca1−H1b = 2.4651, B1−H3 = 1.0598, B1−H1b = 1.1340, B1−H1a = 1.1547; O1−Ca1−O1^i = 180.0, N1−Ca1−B1 = 65.15(5), N1−Ca1−P1 = 29.28(3), P1−Ca1−B1 = 36.15(4), N1−P1−B1 = 108.18(8), H1a−B1-H1b = 105.3, N1−Ca1−H1a = 74.4, N1−Ca1−H1b = 77.3, P1−Ca1−H1a = 50.0, P1−Ca1−H1b = 49.2, B1−Ca1−H1a = 23.8, B1−Ca1−H1b = 23.2, H1b−Ca1−H1b = 43.0, P1−Ca1−P1^i = 180.000(14), N1−Ca1−N1^i = 180.0, B1−Ca1−B1^i = 180.000(1).

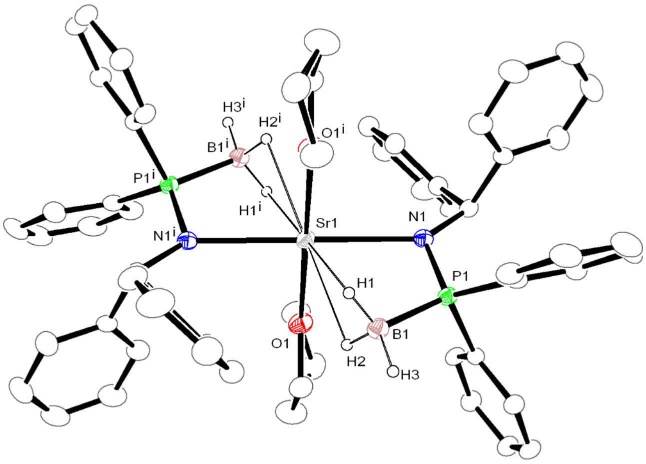


Figure 6. ORTEP drawing of **6** with thermal displacement parameters drawn at the 30% probability level. Hydrogen atoms (except H1, H2, H3 and H1^i, H2^i, H3^i) are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): P1−N1 = 1.623(5), P1−B1 = 1.915(7), P1−Sr1 = 3.3849(13), N1−Sr1 = 2.591(4), B1−Sr1 = 2.995(6), Sr1−O1 = 2.626(4), Sr1−H1 = 2.70(6), Sr1−H2 = 2.60(7), B1−H1 = 1.11(6), B1−H2 = 1.12(7), B1−H3 = 1.14(7); O1−Sr1−O1^i = 180.0, N1−Sr1−B1 = 61.60(16), N1−Sr1−P1 = 27.65(10), P1−Sr1−B1 = 34.24(13), N1−P1−B1 = 108.8(3), H1−B1−H2 = 104(4), H1−B1−H3 = 111(5), H2−B1−H3 = 110(5), B1−Sr1−H1 = 21.6(13), B1−Sr1−H2 = 21.5(15), P1−Sr1−H1 = 49.2(12), P1−Sr1−H2 = 45.2(14), N1−Sr1−H1 = 73.1(12), N1−Sr1−H2 = 71.7(14), P1−Sr1−P1^i = 180.00(5), N1−Sr1−N1^i = 180.0, B1−Sr1−B1^i = 180.0(2).

in comparison to that of the ligand **1-H** (1.918(6) Å), even after the coordination of the BH_3 group to the calcium center.

In compound **6**, the strontium atom is hexacoordinated by two borane groups, two amido nitrogen atoms of two **1** ligands, and two coordinating THF molecules. The solvated THF molecules are trans to each other, and the strontium atom adopts a distorted-octahedral geometry. In comparison to the P–Ca distance (3.2308(4) Å) in compound **5**, the considerably elongated P–Sr distance of 3.385(2) Å, which is also longer than the sum of the covalent radii (3.25 Å) of the phosphorus and strontium atoms, indicates no interaction between the phosphorus and the metal atom. A dihedral angle of 10.65° is observed between the planes formed by the P1, B1, and Sr1 and the P1, N1, and Sr1 atoms, which indicates a slight deviation from coplanarity by the P1, B1, N1, and Sr1 atoms. The strontium–nitrogen bond distance (2.591(14) Å) corresponds well with the distances (2.6512(2) and 2.669(2) Å) in our previously reported strontium complex $[(\mathrm{Imp^{Dipp}})_2\mathrm{Sr(THF)}_3]$ ($\mathrm{Imp^{Dipp}}$ = 2,6-$^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{N{=}CHC}_4\mathrm{H}_3\mathrm{N}$).[9d] The borane ($BH_3$) group is coordinated through the hydrogen atoms in a η^2 fashion and has a Sr1–B1 bond length of 2.995(6) Å, which is longer than in the calcium complex (2.850(2) Å) due to the greater ionic radius of strontium in comparison to calcium. However, the Sr1–B1 distance (2.995(6) Å) is slightly longer than the reported values (2.893(4) and 2.873(4) Å) observed for $[[(\mathrm{Me_3Si})_2\{\mathrm{Me_2(BH_3)P}\}\mathrm{C}]_2\mathrm{Sr(THF)}_5]$.[31]

In accordance with complexes **5** and **6**, the barium amidophosphine–borane complex **7** also crystallizes in the triclinic space group $P\bar{1}$, having one molecule of **7** and two THF molecules in the unit cell. The details of the structural parameters are given in Table S1 in the Supporting Information. The solid-state structure of complex **7** is given in Figure 7. Similar to the calcium and strontium complexes, the coordination polyhedron of the barium complex **7** is formed by two $\{\mathrm{Ph_2P(BH_3)N(CHPh_2)}\}^-$ ligands and two trans THF molecules. As expected because of the larger atomic radius of Ba^{2+},[32,33] the Ba1–N1 (2.733(6) Å), Ba1–O1 (2.790(5) Å), and Ba1–P1 (3.527 (2) Å) distances are elongated in comparison with the corresponding values determined for the Ca^{2+} and Sr^{2+} complexes **5** and **6**, respectively. The considerably elongated P–Ba distance of 3.527(2) Å in **7**, which is greater than the sum of the covalent radii of barium and phosphorus (3.34 Å), indicates that barium and phosphorus have no interaction between themselves. Thus, the central atom barium adopts a distorted-pseudo-octahedral geometry due to the ligation from two **1** moieties and two THF molecules. This high distortion can be mainly attributed to the coordination of adjacent atoms present in the ligand and is indicated by the large N1–Ba1–B1 angle of 58.78(19)°. The borane (BH_3) group is coordinated through the hydrogen atoms in a η^2 fashion and has a Ba1–B1 bond length of 3.159(9) Å. In complex **7**, a dihedral angle of 12.24° is observed between the planes containing P1, B1, and Ba1 and P1, N1, and Ba1 atoms, which indicates a slight deviation from planarity by the P1, N1, B1, and Ba1 atoms. The slight increase in the dihedral angle (12.24°) for **7** in comparison to **5** (10.11°) and **6** (10.65°) can be attributed to the larger ionic radius of barium in comparison to the calcium and the strontium atoms. The Ba1–N1 distance of 2.733(6) Å is similar to the barium–nitrogen covalent bond lengths of 2.720(4) and 2.706(4) Å reported for $[\mathrm{Ba}((\mathrm{Dipp})_2\mathrm{DAD})(\mu\text{-I})(\mathrm{THF})_2]_2$ ($\mathrm{Dipp_2DAD}$ = bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene) in the literature[10] and is also similar to that (2.776(6) Å) of our recently reported complex $[\mathrm{Ba(THF)}_2\{\mathrm{Ph_2P(Se)N(CHPh_2)}\}_2]$ using the analogous phosphine selenoic amido ligand.[11c] It is noteworthy that the P1–B1 distance (1.927(8) Å) remains almost unperturbed in comparison to that of the ligand **1-H** (1.918(6) Å) even after the coordination of the BH_3 group to the barium center. The Ba1–B1 bond length of 3.159(9) Å is the longest among the metal–B distances of **5**–**7** due to barium having the largest ionic radius among Ca, Sr, and Ba. However, the Ba1–B1 distance (3.159(9) Å) is similar to the reported values (3.027(8) and 3.023(8) Å) observed for $[[(\mathrm{Me_3Si})_2\{\mathrm{Me_2(BH_3)P}\}\mathrm{C}]_2\mathrm{Ba(THF)}_5]$.[31]

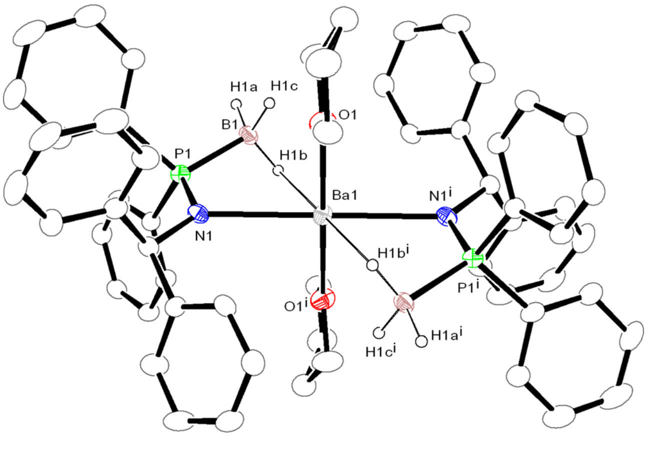


Figure 7. ORTEP drawing of **7** with thermal displacement parameters drawn at the 30% probability level. Hydrogen atoms (except H1a, H1b, H1c and H1a^i, H1b^i, H1c^i) are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): P1–N1 = 1.617(6), P1–B1 = 1.927(8), P1–Ba1 = 3.5273(18), N1–Ba1 = 2.733(6), B1–Ba1 = 3.159(9), Ba1–O1 = 2.790(5), Ba1–H1b = 2.77(7), B1–H1a = 1.21(7), B1–H1b = 1.13(8), B1–H1c = 1.19(10); O1–Ba1–O1^i = 180.0, N1–Ba1–B1 = 58.78(19), N1–Ba1–P1 = 26.22(12), P1–Ba1–B1 = 32.92(15), N1–P1–B1 = 110.4(3), P1–B1–Ba1 = 84.1(3), P1–B1–H1a = 113(3), P1–B1–H1b = 107(4), N1–Ba1–H1b = 70.3(15), H1a)–B1–H1c = 105(6), H1b–B1–H1c = 115(6), P1–Ba1–P1^i = 180.0, N1–Ba1–N1^i = 180.0, B1–Ba1–B1^i = 179.999(1).

CONCLUSION

With this contribution, we have demonstrated a new concept for the design of amidophosphine–borane alkali-metal and alkaline-earth-metal complexes by employing the monoanionic amidophosphine–borane ligand **1**, which forms stable chelating complexes with alkali metals and alkaline-earth metals using three different coordinating atoms and groups adjacent to each other. The strong electron-donating capacity of the N, P, and BH_3 moieties effectively stabilizes the unusual three-membered or four-membered metallacycles. Further studies of complexes **5**–**7** in P-stereogenic building blocks and rare-earth and transition-metal complexes with other amidophosphine–boranes will be published in due course.

EXPERIMENTAL SECTION

General Procedure. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual-manifold Schlenk line interfaced with a high-vacuum (10^{-4} Torr) line or in an argon-filled M. Braun glovebox. THF was predried over Na wire and distilled under nitrogen from sodium and benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$ and stored in the glovebox. ^1H (400 MHz), $^{13}C\{^1H\}$ (100 MHz), $^{11}B\{^1H\}$ (128.4 MHz), and $^{31}P\{^1H\}$ NMR (161.9 MHz) spectra were recorded on a Bruker AVANCE III-400 spectrometer. A Bruker ALPHA FT-IR instrument was used for the FT-IR measurements. Elemental analyses were performed on a Bruker EURO EA instrument at the Indian Institute of Technology Hyderabad. Sodium and potassium bis(trimethylsilyl)amides were purchased from Sigma Aldrich and used as received. The phosphine amine $[Ph_2PNH(CHPh_2)]$[11] and $[M\{N(SiMe_3)_2\}_2(THF)_2]$ (M = Ca, Sr, Ba)[34] compounds were prepared according to the literature procedures by using the respective metal diiodides and $[KN(SiMe_3)_2]$. $[BH_3{\cdot}SMe_2]$ and the NMR solvents $CDCl_3$ and C_6D_6 were purchased from Sigma Aldrich and dried by either molecular sieves ($CDCl_3$) or a Na/K alloy (C_6D_6) prior to use.

Preparation of $[Ph_2P(BH_3)NH(CHPh_2)]$ (1-H). In a predried Schlenk flask was placed 1.0 g (2.72 mmol) of *N*-benzhydryl-1,1-diphenylphosphinoamine in 10 mL of toluene, and to this was added borane−dimethyl sulfide (0.26 mL, 2.72 mmol) in 5 mL of toluene dropwise with stirring at room temperature. The reaction mixture was then stirred for another 12 h. A white precipitate was formed and was filtered through a G4 frit and dried in vacuo. Pure compound was obtained after washing with pentane. Yield: 1.20 g (100%). Compound **1-H** was soluble in $CDCl_3$, CH_2Cl_2, THF, and hot toluene. It was recrystallized from hot toluene. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44−7.49 (m, 4H, ArH), 7.34−7.38 (m, 2H, ArH), 7.24−7.28 (m, 4H, ArH), 7.05−7.19 (m, 10H, ArH), 5.45 (d, 1H, J = 9.4 Hz, CH), 2.83 (br, 1H, NH), 1.17 (br, 3H, BH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 143.5 (ArC), 143.4 (ArC), 132.1 (P attached ArC), 131.9 (P attached ArC), 131.2 (P attached *o*-ArC), 131.1 (P attached *o*-ArC), 128.5 (P attached *p*-ArC), 128.4 (P attached *m*-ArC), 128.3 (*m*-ArC), 127.3 (*o*-ArC), 127.1 (*p*-ArC), 60.8 (CH) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$): δ 56.8 (d, J = 85.8 Hz) ppm. $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$): δ −38.1 (d) ppm. FT-IR (selected frequencies): ν 3338 (N−H), 1434 (P−C), 999 (P−N), 2383 (B−H), 602 (P−B) cm^{-1}. Anal. Calcd for $C_{25}H_{25}BNP$ (381.24): C, 78.76, H, 6.61; N, 3.67. Found: C, 78.30; H, 6.38; N, 3.22.

Preparation of $[(\eta^2\text{-}Ph_2CHNP(BH_3)Ph_2)Li(THF)_2]$ (2). In a 10 mL sample vial 1 equiv (100 mg, 0.264 mmol) of ligand **1-H** and 1 equiv of $LiCH_2SiMe_3$ (25.0 mg, 0.264 mmol) were mixed together with a small amount of THF (2 mL). After 6 h of stirring, a small amount of *n*-pentane (2 mL) was added to the solution, and it was stored at −40 °C. After 12 h, colorless crystals of **2** were obtained. Yield: 120 mg (85%). ^1H NMR (400 MHz, C_6D_6): δ 7.53−7.58 (m, 4H, ArH), 7.06−7.10 (m, 4H, ArH), 6.81−6.90 (m, 12H, ArH), 5.41 (d, J = 21.5 Hz, 1H, CH), 1.45 (br, 3H, BH_3), 3.32 (br, THF), 1.17 (br, THF) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 146.8 (ArC), 146.7 (ArC), 135.7 (P attached ArC), 135.2 (P attached ArC), 132.9 (P attached *o*-ArC), 129.8 (P attached *p*-ArC), 129.1 (P attached *m*-ArC), 128.5 (*m*-ArC), 127.8 (*o*-ArC), 126.5 (*p*-ArC), 68.4 (THF), 66.1 (CH), 25.7 (THF) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ 71.1 (d) ppm. $^{11}B\{^1H\}$ NMR (128.4 MHz, C_6D_6): δ −36.06 (d) ppm. FT-IR (selected frequencies): ν 3373 (N−H), 2382 (B−H), 1447 (P−C), 931 (P−N), 617 (P−B) cm^{-1}. Anal. Calcd for $C_{33}H_{40}BLiNO_2P$ (531.40): C, 74.59; H, 7.59; N, 2.64. Found: C, 74.19; H, 7.44; N, 2.43.

Preparation of $[\{(\eta^3\text{-}Ph_2CHNP(BH_3)Ph_2)Na(THF)_2\}_2]$ (3). In a 10 mL sample vial, 50 mg (0.132 mmol) of ligand **1-H** and 24.2 mg (0.132 mmol) of sodium bis(trimethylsilyl)amide were mixed together with a small amount of THF (2 mL), and the mixture was then stirred for 6 h. A small amount of *n*-pentane (2 mL) was added on top of the solution, and it was stored at −40 °C. After 24 h, colorless crystals of **3** were obtained. Yield: 65 mg (90%). ^1H NMR (400 MHz, C_6D_6): δ 7.65−7.70 (m, 4H, ArH), 7.21−7.23 (d, 4H, ArH), 6.95−7.00 (m, 12H, ArH), 5.46 (d, 1H, J = 25.0 Hz, CH), 3.35 (br, THF), 0.94−1.49 (m, 3H, BH_3), 1.22 (br, THF) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 148.3 (ArC), 148.2 (ArC), 136.7 (P attached ArC), 136.3 (P attached ArC), 130.1 (P attached *o*-ArC), 126.5 (P attached *p*-ArC), 125.9 (P attached *m*-ArC), 125.3 (*m*-ArC), 125.1 (*o*-ArC), 123.2 (*p*-ArC), 65.4 (THF), 62.8 (CH), 22.9 (THF) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ 46.2 (d, J_{PB} = 135.9 Hz) ppm. $^{11}B\{^1H\}$ NMR (128.4 MHz, C_6D_6): δ −34.2 (d) ppm. FT-IR (selected frequencies): ν 3330 (N−H), 2379 (B−H), 1440 (P−C), 929 (P−N), 610 (P−B) cm^{-1}. Anal. Calcd for $C_{66}H_{80}B_2N_2Na_2O_4P_2$ (1094.86): C, 72.40; H, 7.36; N, 2.56. Found: C, 71.98; H, 7.05; N, 2.43.

Preparation of $[\{(\eta^3\text{-}Ph_2CHNP(BH_3)Ph_2)K(THF)_2\}_2]$ (4). In a 10 mL sample vial, 1 equiv of ligand **1-H** (50 mg, 0.132 mmol) and 1 equiv of potassium bis(trimethylsilyl)amide (26.2 mg, 0.132 mmol) were mixed together with a small amount of THF (2 mL). After 6 h, a small amount of *n*-pentane (2 mL) was added to the solution, and it was stored at −40 °C. After 24 h, colorless crystals of **4** were obtained. Yield: 66.9 mg (90%). ^1H NMR (400 MHz, C_6D_6): δ 7.58 (m, 6H, ArH), 6.96−7.01 (m, 14H, ArH), 5.73 (d, J_{HP} = 21.5 Hz, 1H, CH), 3.55 (br, THF), 1.42 (br, THF), 1.82 (br m, 3H, BH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 146.4 (ArC), 144.3 (ArC), 132.3 (P-ArC), 132.2 (P-ArC), 130.7 (P attached *o*-ArC), 128.4 (P attached *p*-ArC), 128.3 (P attached *m*-ArC), 128.2 (*m*-ArC), 127.9 (*o*-ArC), 127.2 (*p*-ArC), 67.6 (THF), 59.9 (CH) 25.6 (THF) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ 73.2 ppm. $^{11}B\{^1H\}$ NMR (128.4 MHz, C_6D_6): δ −37.4 (d) ppm. FT-IR (selected frequencies): ν 3328 (N−H), 2380 (B−H), 1435 (P−C), 999 (P−N), 607 (P−B) cm^{-1}. Anal. Calcd for $C_{66}H_{80}B_2K_2N_2O_4P_2$ (1126): C, 70.33; H, 7.15; N, 2.49;. Found: C, 70.03; H, 6.89; N, 2.21.

Preparation of $[M(THF)_2\{Ph_2P(BH_3)N(CHPh_2)\}_2]$ (M = Ca (5), Sr (6), Ba (7)). *Complex 5. Route 1.* In a 10 mL sample vial, 2 equiv of ligand **1-H** (100 mg, 0.264 mmol) and 1 equiv of $[Ca(N(SiMe_3)_2(THF)_2]$ (40.4 mg, 0.132 mmol) were mixed together with a small amount of THF (2 mL). After 12 h, a small amount of *n*-pentane (2 mL) was added, and it was stored in a −40 °C freezer. After 24 h, colorless crystals of **5** were obtained. Yield: 123 mg (86%).

Route 2. In a 25 mL predried Schlenk flask, a potassium salt of ligand **1-H** (200 mg, 0.32 mmol) was mixed with CaI_2 (46.8 mg, 0.16 mmol) in 10 mL of THF solvent at ambient temperature, and the solution was continuously stirred for 12 h. The white precipitate of KI was filtered off, and the filtrate was dried in vacuo. The resulting white compound was further purified by washing it with pentane, and crystals suitable for X-ray analysis were grown from a THF and *n*-pentane solvent mixture (1:2 ratio) at −40 °C. Yield: 160 mg (92%). ^1H NMR (400 MHz, C_6D_6): δ 7.60−7.65 (m, 4H, ArH), 7.35−7.37 (d, 4H, ArH), 6.80−6.98 (m, 12H, ArH), 5.49 (d, 1H, J = 23.3 Hz, CH), 1.62 (br, 3H, BH_3), 3.32 (br, THF), 1.17 (br, THF) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 148.7 (ArC),148.6 (ArC), 136.3 (P attached ArC), 135.8 (P attached ArC), 132.9 (P attached *o*-ArC), 132.8 (P attached *o*-ArC), 129.8 (P attached *p*-ArC), 128.5 (P attached *m*-ArC), 128.2 (*m*-ArC), 127.9 (*o*-ArC), 125.9 (*p*-ArC), 68.2 (THF) 66.1 (CH), 25.3 (THF) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ 46.9 (d, J = 121.4 Hz) ppm. $^{11}B\{^1H\}$ NMR (128.4 MHz, C_6D_6): δ −31.8 (d) ppm. FT-IR (selected frequencies): ν 3373 (N−H), 1443 (P−C), 972 (P−N), 2380 (B−H), 610 (P−B) cm^{-1}. Anal. Calcd for $C_{66}H_{80}B_2CaN_2O_4P_2$ (1088.96): C, 72.79; H, 7.40; N, 2.57. Found: C, 72.57; H, 7.24; N, 2.21.

Complex 6. In a 10 mL sample vial, 2 equiv of ligand **1-H** (100 mg, 0.264 mmol) and 1 equiv of $[Sr(N(SiMe_3)_2(THF)_2]$ (53.9 mg, 0.132 mmol) were mixed together with a small amount of THF (2 mL). After 12 h, a small amount of *n*-pentane (2 mL) was added to it, and it was stored in a −40 °C freezer. After 24 h, colorless crystals of **6** were obtained. Yield: 136 mg (91%). ^1H NMR (400 MHz, C_6D_6): δ 7.63−7.68 (m, 4H, ArH), 7.24−7.26 (d, 4H, ArH), 6.82−6.96 (m, 12H, ArH), 5.53 (d, 1H, J = 24.5 CH), 1.63 (br, 3H, BH_3), 3.45 (br, THF), 1.29 (br, THF) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 144.1 (ArC),144.0 (ArC), 133.1 (P-ArC), 133.0 (P-ArC), 132.5 (P attached *o*-ArC), 132.3 (P attached *o*-ArC), 131.1 (P attached *p*-ArC), 131.0 (P attached *p*-ArC), 128.6 (P attached *m*-ArC), 128.3 (*m*-ArC), 128.0 (*o*-ArC), 127.2 (*p*-ArC), 68.4 (THF) 61.1 (CH), 25.7 (THF) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ 46.3 ppm. $^{11}B\{^1H\}$ NMR (128.4 MHz, C_6D_6): δ −31.7 (d) ppm. FT-IR (selected frequencies): ν 3376 (N−H), 1444 (P−C), 930 (P−N), 2380 (B−H), 610 (P−B) cm^{-1}. Anal. Calcd for $C_{66}H_{80}B_2N_2O_4P_2Sr$ (1136.50): C, 69.75; H, 7.09; N, 2.46. Found: C, 69.35; H, 6.86; N, 2.32.

Complex 7. In a 10 mL sample vial, 2 equiv of ligand **1-H** (100 mg, 0.264 mmol) and 1 equiv of $[Ba\{N(SiMe_3)_2\}(THF)_2]$ (79.5 mg, 0.132

mmol) were mixed together with a small amount of THF (2 mL). After 12 h of stirring, a small amount of *n*-pentane (2 mL) was added to the reaction mixture, and it was stored in a −40 °C freezer. After 24 h, colorless crystals of **7** were obtained. Yield: 147 mg (94%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.58−7.63 (m, 4H, ArH), 7.25−7.26 (d, 4H, ArH), 7.02−7.06 (m, 12H, ArH), 5.48 (d, 1H, J = 22.3 Hz, CH) ppm, 1.72 (br, 3H, BH_3), 3.38 (br, THF), 1.24 (br, THF) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 148.7 (ArC), 134.5 (P attached ArC), 132.8 (P attached *o*-ArC), 132.6 (P attached *o*-ArC), 129.4 (P attached *p*-ArC), 128.9 (P attached *m*-ArC), 128.1 (*m*-ArC), 127.6 (*o*-ArC), 126.1 (*p*-ArC), 68.2 (THF) 66.5 (CH), 25.3 (THF) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 46.9 ppm. ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): δ −30.9 (d) ppm. FT-IR (selected frequencies): ν 3328 (N−H), 1449 (P−C), 929 (P−N), 2378 (B−H), 603 (P−B) cm^{-1}. Anal. Calcd for $C_{66}H_{80}B_2BaN_2O_4P_2$(1186.22): C, 66.82; H, 6.80; N, 2.36. Found: C, 66.44; H, 6.33; N, 2.09.

Single-Crystal X-ray Structure Determinations. Single crystals of compounds **1-H** were grown from a solution of hot toluene, and compounds **2**−**7** were grown from a THF and pentane mixture at −40 °C under an inert atmosphere. In each case a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 150(2) K. All measurements were made on an Oxford Supernova X-calibur Eos CCD detector with graphite-monochromated Cu Kα (1.54184 Å) or Mo Kα (0.71069 Å) radiation. Crystal data and structure refinement parameters are summarized in Table S1 (Supporting Information). The structures were solved by direct methods (SIR92)[35] and refined on F^2 by full-matrix least-squares methods using SHELXL-97.[36] Non-hydrogen atoms were anisotropically refined. All hydrogen atoms were located in the difference Fourier map and subsequently refined. The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1/[\sigma^2 (F_o^2) + (a\mathrm{P})^2 + b\mathrm{P}]$), where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The functions R1 and wR2 were $(\sum||F_o| - |F_c||)/\sum|F_o|$ and $[\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecules. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 923123−923129. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, + (44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files and a table giving X-ray crystallographic data for **1-H** and **2**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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